

# *Ab initio* many-body calculations of static dipole polarizabilities of linear carbon chains and chain-like boron clusters

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In this paper we report a theoretical study of the static dipole polarizability of two one-dimensional structures: (a) linear carbon chains  $C_n$  ( $n = 2 - 10$ ) and (b) ladder-like planar boron chains  $B_n$  ( $n = 4 - 14$ ). The polarizabilities of these chains are calculated both at the Hartree-Fock and the correlated level by applying accurate *ab initio* quantum chemical methods. Methods such as restricted Hartree-Fock, multi-configuration self-consistent field, multi-reference configuration-interaction method, Möller-Plesset second-order perturbation theory, and coupled-cluster singles, doubles and triples level of theory were employed. Results obtained from *ab initio* wave-function-based methods are compared with the ones obtained from the density-functional theory. For the clusters studied, directionally averaged polarizability per atom for both the systems is seen to increase with the chain size.

## I. INTRODUCTION

The role that atomic and molecular clusters will play in future nanotechnologies is indisputable.<sup>1,2</sup> The experimental progress in this field has been breathtaking, and novel applications have been found in areas such as molecular transport and optoelectronics.<sup>1,2,3</sup> However, theoretical research in this area can also play a very important role in that, by undertaking calculations on clusters of different types, it can help the experimentalists in identifying novel structures for investigation. *Ab initio* calculations on structural and electronic properties of atomic clusters are frequently performed, and the results are put to test in the experiments.<sup>4</sup> One such property of clusters is their electric-dipole polarizability whose experimental and theoretical determination is an area of intense research.<sup>1</sup> The measurements of dipole polarizability are frequently used by the experimentalists to characterize the nature of atomic and molecular species.<sup>1</sup> It describes the response of the electron cloud of the given molecular system to the presence of a d.c. electric field, and thus is easily amenable to experiments. Since the static polarizabilities are the zero-frequency limits of the corresponding dynamic quantities, they also provide information about the response of the system to off-resonant a.c. fields. Most of the

theoretical calculations of both the structural and electronic properties such as static polarizabilities of atomic clusters are performed within the framework of the density functional theory (DFT). Despite the fact that DFT has enjoyed indisputable success in solid state physics and quantum chemistry as a computationally cheap routine tool for large-scale investigations, it has the drawback that results depend highly on the chosen functional, and cannot be improved in a systematic way. Wavefunction-based *ab initio* quantum-chemical techniques on the other hand are free from this flaw, and provide a large array of methods of different accuracy and computational cost. Moreover, the prediction of reliable values of dipole polarizabilities and hyperpolarizabilities by rigorous quantum chemical methods has made significant contributions, and added new vigor, to the search of novel optical materials<sup>3,4</sup>. Thus, in order to obtain reliable estimates for dipole polarizabilities, and also to cross check the DFT-based results, it is worthwhile to investigate the electron correlation effects in a systematic way by using the quantum-chemical many-body techniques. In this work, we present fully size-consistent *ab initio* calculations to the static dipole polarizability of linear carbon clusters  $C_n$  ( $n = 2 - 10$ ) and chain-like boron clusters  $B_{2n}$  ( $n = 2 - 7$ ), of increasing size. The reason behind our focus on one-dimensional structures is that quantum confinement due to reduced dimensions, combined with the possible delocalization of the electrons along the backbone, can lead to enhanced linear and nonlinear susceptibilities of these structures, as compared to their three-dimensional counterparts. In the present study, the electron-correlation effects have been taken into account by various size-consistent methods: multi-reference configuration interaction, second-order Möller-Plesset perturbation theory, coupled-cluster singles and doubles (CCSD), and coupled-cluster singles and doubles with the perturbative treatment of the triples (CCSD(T)). All earlier calculations on these systems, with the exception of  $B_4$ , were performed within the framework of DFT, with which we compare our results. Next, we briefly review the state-of-the-art of research on these two types of clusters.

Carbon clusters have been the subject of research for decades as possible key materials for future nanotech-

nologies<sup>2</sup>. For the smaller systems, up to and including those containing nine atoms, linear neutral, positively and negatively charged clusters are generated and detected in experiments<sup>5</sup>. The structures and energetics of linear carbon clusters are well studied by employing coupled-cluster approaches.<sup>6,8</sup> Recently, we studied the ground state of an infinite carbon chain at the *ab initio* level using various many-body approaches including CCSD(T).<sup>9</sup> Lou et al. have investigated the influence of an electric field on the energetic stability of linear carbon chains<sup>10</sup>. Recently Fuentealba<sup>11</sup> has calculated the static dipole polarizabilities of carbon chain using density functionals of the hybrid type in combination with the finite-field method. He showed that dipole polarizabilities are an important quantity for the identification of clusters with different numbers of atoms and even for the separation of isomers. Here we compare our many-body-methods based polarizabilities with those computed by Fuentealba<sup>11</sup> using the DFT approaches.

Boron is a trivalent element with the valence shell configuration  $s^2p^1$ . Although compared to carbon, the valence shell of boron is electron deficient, it still exhibits  $sp^2$  hybridization with strong directional chemical bonds.<sup>12</sup> In composite materials, for small content, boron tends to form a linear chain, while as its content increases it can form structures ranging from two- to three-dimensional.<sup>12</sup> As far as isolated clusters containing boron are concerned, experimentally, they have been studied by Anderson and coworkers,<sup>13</sup> and by La Placa et al.<sup>14</sup> In addition, Chopra et al.<sup>15</sup> and Lee et al.<sup>16</sup> have experimentally synthesized the boron-nitrogen nanotubes and cage-like boron-nitrogen structures. Several authors have also reported theoretical calculations on the boron clusters.<sup>17,18,19,20,21,22,23,24,25,26,27,28,29,30</sup> Boustani et al.<sup>21</sup> have shown theoretically that, similar to carbon, boron has a strong potential to form stable nanotubular structures. Boustani and coworkers recently studied small cationic<sup>22</sup> and neutral boron clusters<sup>23</sup> and obtained structures that are fundamentally different from crystal subunits of the well-known  $\alpha$ - and  $\beta$ - rhombohedral phases of boron, which consist mainly of  $B_{12}$  icosahedra. They classified the boron clusters into four topological groups: convex and spherical<sup>24</sup>, quasipplanar<sup>25</sup> and nanotubular<sup>26</sup>. The quasipplanar and convex structures can be considered as fragments of planar surfaces, and as segments of hollow spheres, respectively. The main focus of their theoretical work has been to ascertain the structures of larger boron clusters in terms of a small number of building blocks.<sup>27,28</sup> However, recently Sabra and Boustani<sup>28</sup> studied the ground-state energetics of ladder-like quasi-one-dimensional clusters of boron by quantum chemical methods. They concluded that such structures are not the lowest in energy. However, because of the proximity of their energy to that of the true ground-state geometries, they can be regarded as metastable states.<sup>28</sup> Thus, with some experimental manipulation, it may be possible to realize such structures in laboratory. Keeping this possibility in mind, we

decided to compute the static polarizabilities of ladder-like quasi-one-dimensional structures of boron by *ab initio* many-body methods. In addition to the quantum-chemical calculations, we also perform the DFT-based calculations of static dipole polarizabilities of these clusters using the same basis set, so as to understand the influence of electron-correlation effects on the polarizabilities of these systems. Recently, Reis and coworkers computed the static dipole polarizabilities of rhombic  $B_4$  using various quantum-chemical methods,<sup>29</sup> and several other boron clusters  $B_n$  ( $n = 3 - 8, 10$ ) within the framework of DFT, employing a variety of exchange-correlation functionals.<sup>30</sup> However, unlike the quasi-one-dimensional geometries considered by us, Reis et al.<sup>30</sup> performed these calculations on the ground-state geometries of Boron clusters optimized earlier by Boustani.<sup>27</sup> We compare our many-body static polarizabilities of various boron clusters to those reported by Reis et al.<sup>29,30</sup> in order to understand the influence of the cluster structures on their static polarizabilities.

The remainder of the paper is organized as follows. In section II, the applied methods and computational details are briefly described. The results are then presented and discussed in section III. Finally, our conclusions are presented in section IV.

## II. METHODS AND COMPUTATIONAL DETAILS

For the closed-shell clusters, first the polarizabilities are calculated by using the restricted Hartree-Fock (RHF) method, and thereafter the electron-correlation effects are included via the Møller-Plesset second-order perturbation theory (MP2), and the coupled-cluster (CC) techniques. For the open-shell clusters, the calculations are initiated by the multi-reference self-consistent-field (MCSCF) method, while the electron-correlation effects are taken into account by the multi-reference configuration-interaction (MRCI) method. In order to calculate static dipole polarizability first we performed calculations without an external electric field, and then we added an external electric field of strength 0.001 a.u. along the  $x$ ,  $y$  and  $z$  axis separately. Stability of the results with respect to the value of the field was carefully examined by performing some calculations for various other values of the field strength. However, when we perform high-level correlated calculations, the expectation value of the dipole moment is not directly available. Therefore, to calculate the static dipole polarizabilities, we have adopted a finite-difference formula in which the diagonal polarizability tensor elements are obtained through the second derivative of the total energy with respect to the external electric field. The field-dependent total energy is used in the following finite-difference formula:

$$\alpha_{jj} = - \left[ \frac{\partial^2 E(\varepsilon_j)}{\partial \varepsilon_j^2} \right]_{\varepsilon=0} = - \lim_{\varepsilon_j \rightarrow 0} \frac{E(\varepsilon_j) + E(-\varepsilon_j) - 2E(0)}{\varepsilon_j^2} = \lim_{\varepsilon_j \rightarrow 0} \frac{E(0) - E(\varepsilon_j)}{\varepsilon_j^2} \quad \text{our results to experiments}$$

where  $E(\varepsilon_j)$  is total energy with respect to field  $\varepsilon_j = 0.001$  a.u. and  $E(0)$  is total energy without field. This equation holds only for centrosymmetric systems.

For the linear carbon chain, assuming the  $z$  axis is the chain direction, we calculated the parallel ( $\alpha_{zz}$ ) and perpendicular ( $\alpha_{xx}$ ) components of the static dipole polarizability. Our calculations are performed using the geometry reported by Watts et al.<sup>8</sup>. Since the ground state of even number of carbon atoms is triplet and of odd number of carbon atoms is singlet we calculated the static dipole polarizabilities of even number of carbon atoms i.e.,  $C_4$ ,  $C_6$ ,  $C_8$  and  $C_{10}$  for its ground state by the MC-SCF and the MRCI methods, whereas for odd number of carbon atoms i.e.,  $C_3$ ,  $C_5$ ,  $C_7$  and  $C_9$  we calculated them by using the RHF, MP2, CCSD, and the CCSD(T) methods. All calculations were performed with the MOLPRO molecular orbital *ab initio* program package<sup>31</sup> by employing Sadlej basis sets<sup>32</sup> which was specially constructed for the calculation of dipole polarizabilities.

For the chain-like boron clusters we assumed that the boron atoms were lying in the  $xy$  plane, with the chain direction along the  $x$ -axis. We first optimized the geometry of each cluster, i.e.,  $B_4$ ,  $B_6$ ,  $B_8$ ,  $B_{10}$ ,  $B_{12}$  and  $B_{14}$  for its ground state at the B3LYP/6-31+G(d) level of approximation by using the GAUSSIAN98 program<sup>33</sup>. The ground state is singlet for  $B_4$ ,  $B_{10}$ ,  $B_{12}$   $B_{14}$  and triplet for  $B_6$ ,  $B_8$ . Then we calculated the parallel ( $\alpha_{xx}$ ), transverse ( $\alpha_{yy}$ ) and perpendicular ( $\alpha_{zz}$ ) components of the static dipole polarizabilities with standard polarized valence double-zeta (VDZ) basis sets at the Hartree-Fock and correlated level e.g., MRCI, MP2, CCSD and CCSD(T) by employing MOLPRO molecular orbital *ab initio* program package<sup>31</sup>. Although the basis set which we used in chain-like boron clusters is a rather small basis set, a larger set would have been computationally too expensive when we prolong the chain. It has been shown further in Ref.<sup>30</sup> that using the larger triple-zeta basis set aug-cc-pVTZ does not have a large effect on the calculated polarizabilities for the cluster  $B_4$ . Therefore, for these clusters the chosen basis set should be sufficient.

### III. RESULTS AND DISCUSSIONS

#### A. Linear carbon clusters

The calculated Cartesian components of static dipole polarizabilities and average polarizabilities  $\alpha_{av} = (\alpha_{zz} + 2\alpha_{xx})/3$  for linear carbon clusters are presented in Table I. Figure 2 presents our calculated polarizabilities per atom, plotted as a function of the number of atoms in the chain ( $N$ ). Additionally, for the sake of comparison,

in the same figure we have also plotted the DFT-based results of Fuentealba<sup>11</sup>. It is not possible for us to compare our results to experiments because of the absence of any polarizability data on the carbon chains. From Fig. 2 it is obvious that parallel component of the static dipole polarizability per atom,  $\alpha_{zz}/N$ , increases roughly linearly from  $C_2$  to  $C_{10}$ , whereas perpendicular components  $\alpha_{xx}/N$  and  $\alpha_{yy}/N$  are essentially constant as a function of  $N$ . As far as the comparison of our results with the DFT results of Fuentealba<sup>11</sup> is concerned, the agreement is generally very good on all components of polarizabilities except for the case of  $N = 2$ . For  $N = 2$ , however, Fuentealba<sup>11</sup> reports an anomalously large value of  $\alpha_{xx}$  (and hence  $\alpha_{xx}/N$ ), making it in disagreement with his values of  $\alpha_{xx}/N$  computed for higher values of  $N$ . From Fig. 2 it is also clear that the directionally-averaged polarizability per atom  $\alpha_{av}/N$ , also shows an overall increase as a function of the chain length. Since polarizability is an extensive quantity, therefore, for very large number of atoms in the chain ( $N \rightarrow \infty$ ),  $\alpha_{av}/N$  should approach its bulk value. However, from our results it is obvious that for  $N = 10$ ,  $\alpha_{av}/N$  is still increasing as a function of  $N$ , exclusively because of the increase in the parallel component  $\alpha_{xx}/N$ . One can understand the increase in  $\alpha_{xx}/N$  as a function of  $N$  on the intuitive grounds based upon the behavior of  $\pi$  electrons.  $\pi$  electrons (of which the carbon chain has two per atom), as against the  $\sigma$  electrons, are highly delocalized along the chain direction. Therefore, it will take much larger cluster sizes before their response to an external field approaches that in the bulk.

The other somewhat surprising aspect of our results for the carbon chains is the generally excellent agreement obtained between the DFT values, and the many-body values of the static polarizabilities. This means that for the static polarizabilities of carbon chains, DFT is able to describe the electron correlation effects quite well. It is also rather interesting to note that MP2 method provides a theoretical description of these clusters quite close to that obtained with the CCSD(T) method. A similar effect was observed by Maroulis<sup>34</sup> in the polarizability calculations of a system composed of two water molecules.

#### B. Chain-like boron clusters

Earlier Sabra et al.<sup>28</sup> had shown that strictly one-dimensional chains of boron are unstable. They demonstrated that boron prefers to form a zig-zag ladder-like quasi-one-dimensional structure.<sup>28</sup> Therefore, in the present work we have concentrated on the identical structures of boron  $B_{2n}$  ( $n = 2 - 7$ ), which, as shown in Fig. 1, can be obtained by adding boron dimers to  $B_4$ , which has a parallelogram structure. First we optimized the ground-state geometry of each of these clusters by employing B3LYP/6-31+G(d) method, and these optimized geometries are given in Fig. 1. From optimization we

found that the system is completely centrosymmetric. The optimized geometries of each cluster are comparable to those obtained by Boustani<sup>27</sup> who optimized the structures of elemental, convex and quasiplanar boron clusters  $B_n$  ( $n = 2 - 14$ ) at the RHF level with the  $3 - 21G$  basis set.

Results of our calculation on longitudinal ( $\alpha_{xx}$ ), transverse ( $\alpha_{yy}$ ), perpendicular ( $\alpha_{zz}$ ), and directionally-averaged polarizabilities  $\alpha_{av} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$  at the HF and correlated level, as well as at the DFT level are presented in table II. The polarizabilities per atom based upon this data are plotted as a function of the number of atoms in the cluster in Fig. 3. An inspection of the table and the figure reveals the following trends: (i) The longitudinal static dipole polarizability per atom  $\alpha_{xx}/N$  increases almost linearly with  $N$ , the component  $\alpha_{yy}/N$  shows a gradual decrease, while  $\alpha_{zz}/N$  exhibits saturation. (ii) For the triplet ground state clusters  $B_6$  and  $B_8$ , the polarizabilities computed by the MCSCF and the MRCI methods are in almost complete agreement indicating that the MCSCF method has already captured the most important correlation effects. (iii) For the remaining clusters whose ground state is singlet, the inclusion of electron correlation effects leads to a reduction of the  $\alpha_{xx}$  component, while the other components are rather unaffected. For example, the CCSD(T) value of  $\alpha_{av}$  for  $B_{14}$  is about 6 % smaller compared to its RHF value. (iv) Similar to the case of carbon chains, for all boron clusters considered here, generally there is very good agreement between the polarizabilities computed by the best wavefunction methods (MRCI and CCSD(T)), and the ones computed using the DFT/B3LYP approach. Thus, in this case also, the DFT is able to account for the electron correlation effects quite well.

Since there are no experimental results for the static dipole polarizabilities for the ladder-like structures of boron, we compare our results to the theoretical results obtained by other authors.<sup>29,30</sup> First considering the case of rhombic  $B_4$ , for the average static dipole polarizability  $\alpha_{av}$ , we obtained 51.99 a.u. for with the CCSD(T) approach while Reis et al.<sup>29</sup> report a CCSD(T) value 60.00 a.u. for the same quantity. The  $\alpha_{xx}$  and  $\alpha_{yy}$  values from our calculations cannot be directly compared to those reported by Reis et al.<sup>29</sup> because of the different orientations of the  $x$  and the  $y$  axes in their calculations. However, for  $\alpha_{zz}$ , whose values can be compared directly, Reis et al.<sup>29</sup> report the value 39.5 a.u., while we obtained 27.12 a.u. for the same quantity. Although the optimized geometries, as well as the basis set used by Reis et al.<sup>29</sup> were somewhat different from ours, we still believe that those factors cannot explain the difference of  $\approx 12$  a.u. in the values of  $\alpha_{zz}$ . However, clearly it is this disagreement—the reasons behind which are not clear to us—which is primarily responsible for the disagreement in the values of  $\alpha_{av}$  observed between our results and those of Reis et al.<sup>29</sup>

Besides  $B_4$ , there are no theoretical results on the larger ladder-like clusters of boron. However, in another

paper Reis et al.<sup>30</sup> reported DFT based calculations of the static polarizabilities of convex and quasiplanar  $B_n$  ( $n = 3 - 10$ ) clusters whose geometries were optimized earlier by Boustani.<sup>27</sup> Therefore, in order to understand the effect of the geometric structure on the polarizabilities of boron clusters, we compare our results on  $B_6$ ,  $B_8$ , and  $B_{10}$ , with the corresponding isomers studied by Reis et al.<sup>30</sup> For  $B_6$  Reis et al.<sup>30</sup> considered a benzene-like hexagonal geometry with the  $D_{2h}$  symmetry, and computed the value  $\alpha_{av} = 101.3$  a.u. For  $B_8$  also Reis et al.<sup>30</sup> considered a ring-like structure with the  $D_{7h}$  symmetry and reported  $\alpha_{av} = 114.6$  a.u. Finally, for  $B_{10}$  they considered a quasiplanar structure with the  $C_{2h}$  symmetry and calculated  $\alpha_{av} = 143.7$  a.u.<sup>30</sup> These can be compared with our DFT values of  $\alpha_{av}$  of the ladder-like  $B_6$ ,  $B_8$ , and  $B_{10}$  which were obtained to be 92.35 a.u., 130.65 a.u., and 185.53 a.u., respectively. From the comparison it is clear that although the polarizability of the benzene-like  $B_6$  is larger than that of the ladder-like  $B_6$ , however, for clusters containing larger number of atoms ( $B_8$  and  $B_{10}$ ) quasi-one-dimensional ladder-like structures are more polarizable than the planar structures. Although, no theoretical results on  $\alpha_{av}$  for the planar structures of  $B_{12}$  and  $B_{14}$  are available, however, it is clear that even for those clusters ladder-like structures will be obtained to be more polarizable. The fact that for larger number of atoms, ladder-like boron chains will be more polarizable than quasiplanar isomeric structures of boron, can be understood based upon intuitive arguments. As Sabra et al.<sup>28</sup> showed by explicit calculations, with the increasing size, the  $\pi$ -electron population of these ladder-like chains increases. Since the  $\pi$ -electrons are quite delocalized along the chain direction, their response to the electric fields directed along the chain direction will be quite large leading to large values of  $\alpha_{xx}$  obtained in our calculations. The fact that  $\alpha_{xx}$  increases quite rapidly with the increasing number of atoms also confirms this hypothesis. Although, the quasiplanar structure of boron also have  $\pi$  electrons due to the  $sp^2$  hybridization, however, their response to the external field is distributed in two directions due to their two-dimensional character, leading to smaller polarizabilities. Therefore, it is the combined effect of  $\pi$  electrons and the reduced dimensionality which makes the ladder-like chains of boron more polarizable than its quasiplanar counterparts.

#### IV. CONCLUSIONS AND FUTURE DIRECTIONS

In conclusion, we have reported a systematic *ab initio* study of the static dipole polarizability of the linear carbon chains and the ladder-like boron chains employing Hartree-Fock, many-body, and the DFT-based approaches. For closed-shell clusters the polarizabilities computed by the RHF method were generally within 5%–6% agreement with the ones computed by the CCSD(T) method. Similarly for the open-shell clusters

the MCSCF polarizabilities were found to be in very good agreement with the ones computed by the MRCI method. Additionally, DFT-based results on the polarizabilities were found to be in very good agreement with the ones computed by the many-body methods. This suggests the possibility that by employing computationally less expensive approaches such as RHF, MCSCF, DFT etc. one can perform similar calculations on even larger and more complex clusters, and obtain reasonable results on static polarizability. We believe that such a line of investigation should be pursued in future calculations.

Our results demonstrate that in both the systems the component of the polarizability along the chain direction, as well as the average polarizability, increase with the chain size. This is fully consistent with presence of the delocalized  $\pi$ -electrons in these one-dimensional clusters. Thus both types of clusters should be useful in nonlinear optical applications as well. Of late, the molecular transport properties of carbon chains have been of much interest to physicists,<sup>35</sup> because of the presence of the delocalized  $\pi$ -electrons in them. However, our polarizability calculations point to the presence of the delocalized  $\pi$ -electrons also in the ladder-like boron clusters, thus rendering them possibly useful in molecular-transport-based applications. First principles studies of the excited states, and the transport properties of such clusters will be the subject of future investigations.

## ACKNOWLEDGMENTS

One of us (A.A.) is grateful to Professor T. Wolff and Graduiertenkolleg Struktur-Eigenschafts-Beziehungen bei Heterocyclen for financial support.

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<sup>33</sup> Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr. J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farksa, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.;

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<sup>34</sup> G. Maroulis, J. Chem. Phys. **113**, 1813 (2000).

<sup>35</sup> See, e.g., N.D. Lang and Ph. Avouris, Phys. Rev. Letts. **84**, 358 (2000), and references therein.

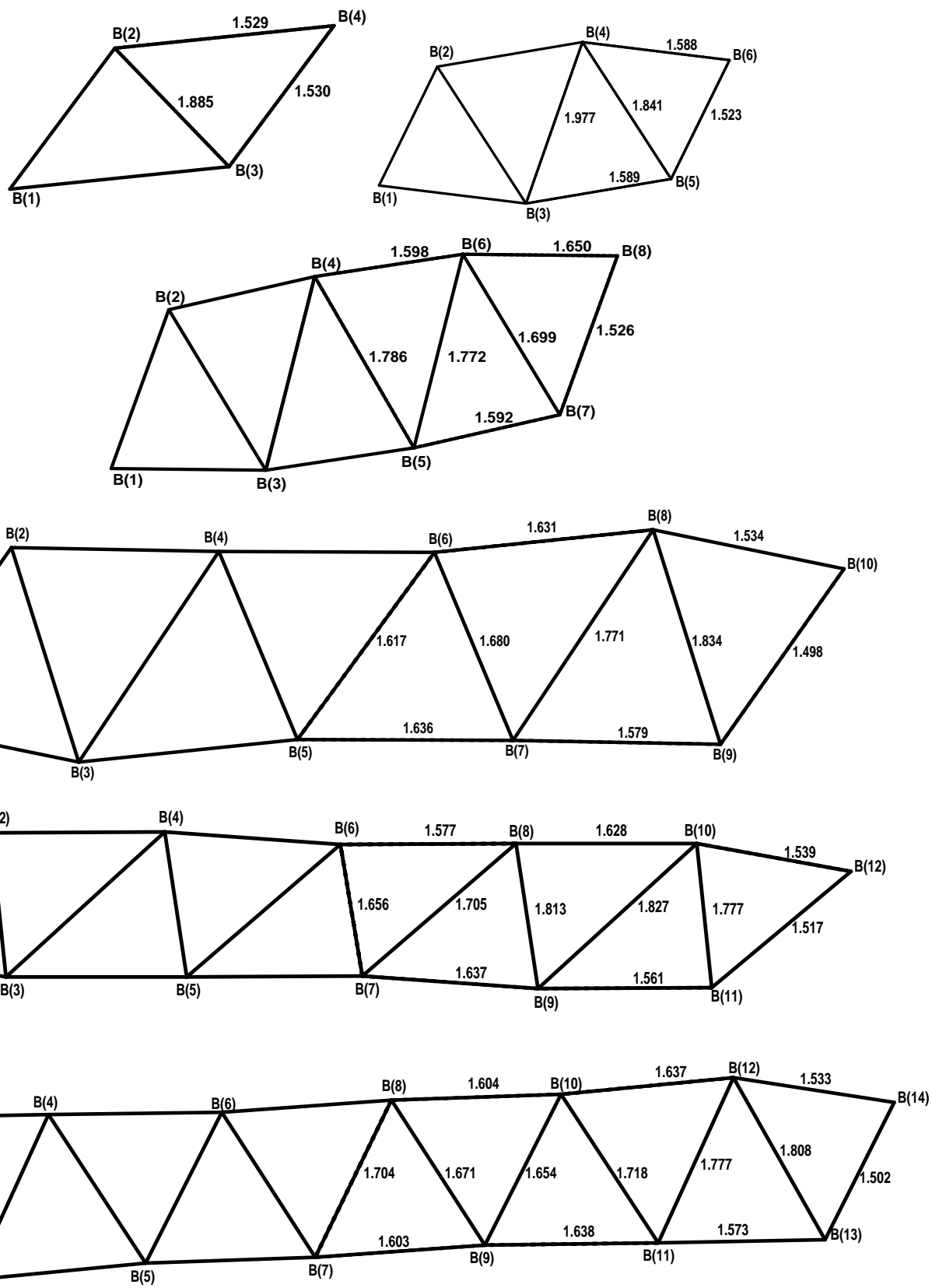


FIG. 1. The chain-like structure of boron clusters.

FIG. 2. The static dipole polarizability per atom of linear carbon clusters. The line has been plotted to guide the eyes.

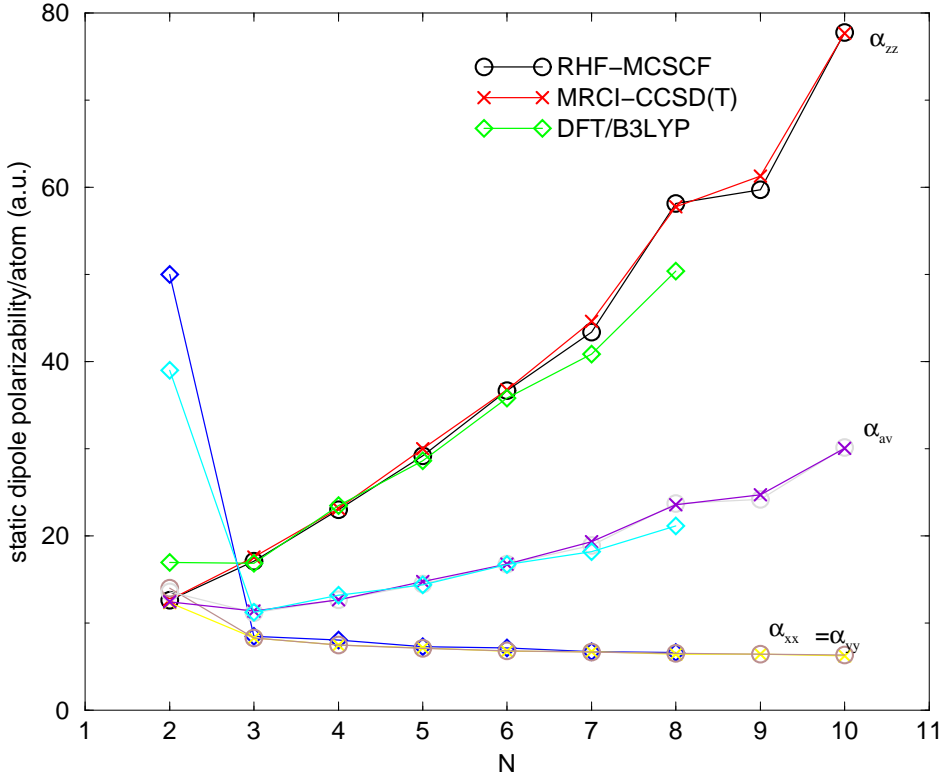


FIG. 3. The static dipole polarizability per atom of chain-like boron clusters. The line has been plotted to guide the eyes.

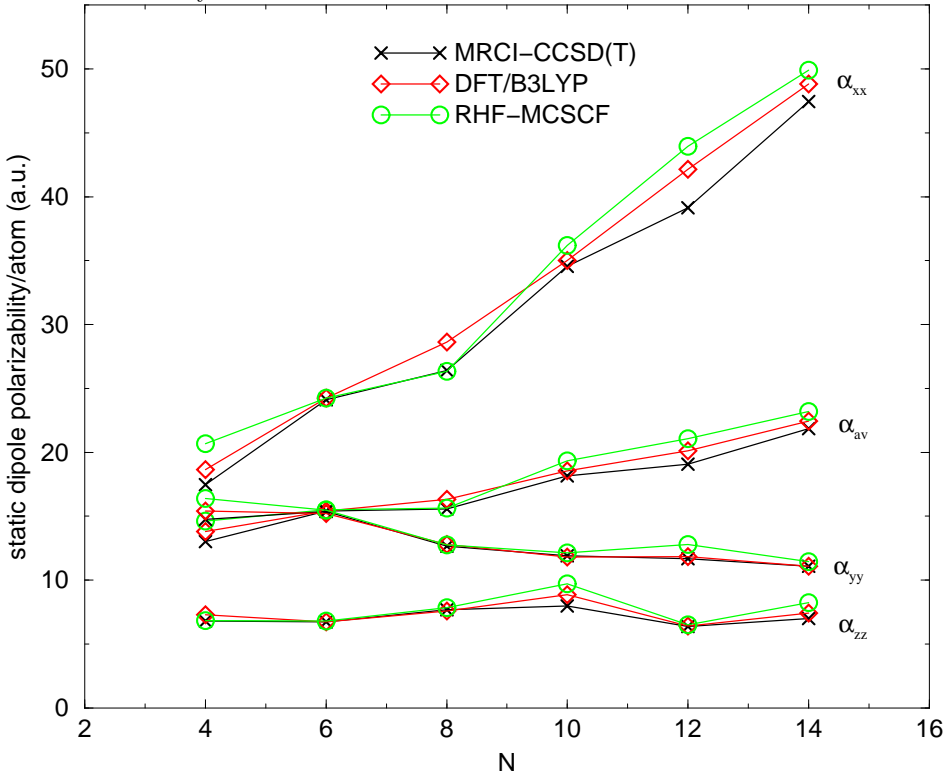




TABLE I. Linear carbon clusters: Static dipole polarizabilities (in a.u.) calculated with the Sadlej basis set.

Atoms	Methods	$\alpha_{xx} = \alpha_{yy}$	$\alpha_{zz}$	$\alpha_{av}$
C <sub>2</sub>	MCSCF	28.00	25.22	27.07
	MRCI	24.57	25.24	24.79
	DFT/B3LYP <sup>a</sup>	100.00	33.90	78.00
C <sub>3</sub>	RHF	24.72	51.16	33.53
	MP2	24.46	51.68	33.53
	CCSD(T)	24.82	52.66	34.10
	DFT/B3LYP <sup>a</sup>	25.30	50.50	33.70
C <sub>4</sub>	MCSCF	29.86	91.88	50.54
	MRCI	29.71	92.38	50.60
	DFT/B3LYP <sup>a</sup>	32.10	93.70	52.60
C <sub>5</sub>	RHF	35.42	145.74	72.19
	MP2	35.38	149.74	73.50
	CCSD(T)	35.50	149.88	73.63
	DFT/B3LYP <sup>a</sup>	36.20	142.90	71.70
C <sub>6</sub>	MCSCF	40.81	219.88	100.50
	MRCI	40.45	220.40	100.44
	DFT/B3LYP <sup>a</sup>	42.80	214.70	100.00
C <sub>7</sub>	RHF	46.54	303.50	132.19
	MP2	46.22	314.80	135.75
	CCSD(T)	46.74	312.30	135.26
	DFT/B3LYP <sup>a</sup>	47.00	285.80	127.00
C <sub>8</sub>	MCSCF	51.82	464.78	189.47
	MRCI	51.34	462.11	188.26
	DFT/B3LYP <sup>a</sup>	52.60	403.00	169.00
C <sub>9</sub>	RHF	57.58	537.12	217.43
	MP2	57.20	555.04	223.15
	CCSD(T)	57.64	551.54	222.27
C <sub>10</sub>	MCSCF	62.85	777.51	301.07
	MRCI	62.29	776.39	300.32

<sup>a</sup> Taken from Ref.<sup>11</sup>.

TABLE II. Chain-like boron clusters: Static dipole polarizabilities (in a.u.) calculated with the VDZ basis set.

Atoms	Methods	$\alpha_{xx}$	$\alpha_{yy}$	$\alpha_{zz}$	$\alpha_{av}$
B <sub>4</sub>	RHF	82.72	65.54	27.30	58.52
	MP2	66.34	57.28	27.30	50.31
	CCSD(T)	69.88	58.98	27.12	51.99
	DFT/B3LYP	74.60	61.60	29.20	55.13
B <sub>6</sub>	MCSCF	145.45	92.86	40.78	93.03
	MRCI	144.64	92.16	40.28	92.36
	DFT/B3LYP	145.51	91.15	40.39	92.35
B <sub>8</sub>	MCSCF	210.72	101.93	62.73	125.12
	MRCI	211.28	101.17	61.54	124.66
	DFT/B3LYP	229.05	102.40	60.51	130.65
B <sub>10</sub>	RHF	361.86	121.24	97.00	193.37
	MP2	362.08	120.86	63.54	182.16
	CCSD(T)	345.70	118.90	79.82	181.47
	DFT/B3LYP	350.20	118.00	88.40	185.53
B <sub>12</sub>	RHF	527.32	153.60	77.90	252.94
	MP2	445.82	129.52	76.04	217.12
	CCSD(T)	469.70	140.06	76.58	228.78
	DFT/B3LYP	505.80	142.20	76.80	241.60
B <sub>14</sub>	RHF	698.90	160.16	115.36	324.81
	MP2	680.52	152.68	75.92	303.04
	CCSD(T)	664.48	155.08	97.66	305.74
	DFT/B3LYP	683.80	155.20	104.00	314.33